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Intramolecular magnesium bonds in malonaldehyde-like systems. A critical view of the resonance-assisted phenomena.

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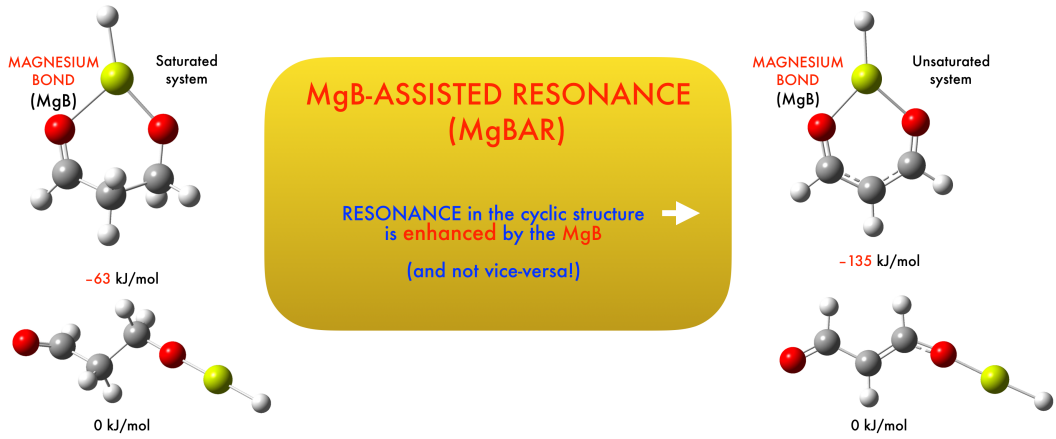
Abstract

Through the use of high-level G4-theory calculations we have investigated the structure, stability and bonding of a set of Mg derivatives formed by replacing the –OH group of malonaldehyde or only the hydrogen atom of this group by a –MgH group. To give insight on the resonance-assisted phenomenon, which might be involved in the stabilization of these compounds, we also included the corresponding saturated analogues in our survey. The effect of the rigidity of the molecular framework was considered by analyzing the Mg-derivatives of (*Z*)-4-(hydroxymethylene)cyclobut-2-enone, obtained through the same substitutions mentioned above. The effect of replacing the carbonyl group by an imino group was also contemplated. In all cases, the global minimum is a cyclic conformer stabilized through the formation of rather strong intramolecular magnesium bonds. The strength of these interactions is directly related with the intrinsic basicity of the carbonyl group (or the imino group) and the intrinsic acidity of the –MgH group, rather than with a resonance-assisted phenomenon. As a matter of fact, for all the investigated systems, the conclusion is that resonance in the cyclic conformer is directly correlated with the strength of the intramolecular magnesium bond, and not vice-versa. Interestingly, the strength and characteristics of these interactions for these Mg-containing derivatives are very similar to those of the corresponding Be-containing analogues.

Keywords: ab initio calculations • Intramolecular interactions • magnesium bonds • beryllium bonds • magnesium-bonding-assisted resonance (MgBAR).

Graphical Abstract



Magnesium derivatives such as CHO-CH=CH-OMgH which can be considered derivatives of malonaldehyde, and their saturated analogues are stabilized through the formation of intramolecular Mg bonds. The unsaturated systems exhibit a magnesium-bond-assisted resonance (MgBAR).

Introduction

The interaction between closed systems plays an important role in chemistry leading to the formation of clusters of molecules of different size and properties.[1] Most of these clusters, if not all, can be seen as the result of a Lewis base-Lewis acid interaction, even when the two interacting systems are identical. A paradigmatic example is the hydrogen bond (HB) that stabilizes the water dimer,[2] in which besides the electrostatic contributions involving both monomers, there is a polarization of one of the molecules, acting as a Lewis base, the hydrogen bond acceptor, to the other molecule, the hydrogen bond donor, acting as a Lewis acid. This effect is reflected in a partial population of the antibonding O–H molecular orbital of the O–H bond directly involved in the formation of the HB. Consistently, this bond experiences a red shifting of its stretching vibrational frequency along with the corresponding elongation.[3] Similar effects can be identified in other closed-shell interactions, but they reach a maximum when involving intrinsically electron-deficient atoms such as Be or B [4, 5].

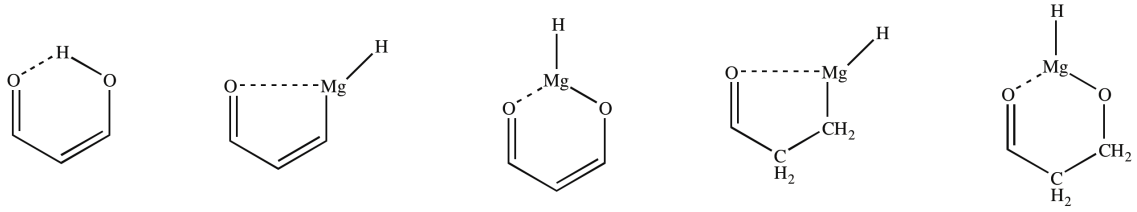
In the particular case of interactions involving BeX_2 derivatives, known as beryllium bonds,[5] the strength of the interaction leads to a significant charge transfer from the lone pairs of the Lewis base to the empty *p* orbitals of the Be atom and to the $\sigma_{Be\text{-}X}$* antibonding orbitals. Coherently, the formation of the beryllium bond involves a significant bending of the BeX_2 subunit, due to the hybridization change undergone by the Be atom when partially populating the initially empty p orbitals of Be, and also a lengthening of the Be-X linkages, through the population of the σ_{BeX}* antibonding orbital.[5]

Another important consequence of these electron density redistributions is cooperativity, which appears nicely reflected, for instance, in the enhanced strength of the HBs of the water trimer,[6, 7] but also in the mutual stabilization of the HBs and the beryllium bond of an imidazole dimer interacting with a BeX_2 molecule.[8] Not surprisingly, very significant effects are also observed in the case of intramolecular beryllium-bonded systems as recently reported in the literature [9]. This question was analyzed using derivatives of malonaldehyde as a model system, in which the H atom of the –OH group or the whole –OH group are replaced by a –BeH group. Rather interestingly this study permitted to shed some light on a controversial question as it is the so-called Resonance-Assisted Hydrogen Bond (RAHB) [9]. RAHB was proposed as a mechanism to explain the strong intramolecular hydrogen bonds in malonaldehyde

and other systems.[10-14] The RAHB idea was questioned later [15-18] suggesting that in malonaldehyde and similar systems what is observed is not an enhancement of the resonance due to the formation of an intramolecular hydrogen bond, but rather a hydrogen bonding enhancement assisted by the resonance in the system, [17-19] what Romero-Fernandez et al. named hydrogen-bonding-assisted resonance (HBAR)[17]. Even more recently interesting cases were described in which a network of conjugated bonds strongly hinders a hydrogen bond, phenomenon which was called Resonance Impaired Hydrogen Bonds (RIHB) [20].

Also recently, it was shown that Mg can also yield magnesium bonds similar to the beryllium ones [21]; but, what is more important and unexpected, in some specific cases the magnesium bonds were found to be of similar strength or even stronger than the beryllium bond analogues [22]. The question we would like to address in this paper is whether the intramolecular magnesium bonds also share some similarities with the corresponding intramolecular beryllium bonds and if some dissimilarities appear, what is the origin.

For this purpose, we decided to investigate, using density functional theory methods and high-level *ab initio* methods as well, the structure and electronic properties of the Mg derivatives formed by replacing i) the –OH group of the enol form of malonaldehyde, (Z)-3-hydroxyprop-2-enal (**1**), ii) only the hydrogen atom of its –OH group by a –MgH group (see structures **1-MgH** and **1-OMgH** in Scheme **I**). In order to provide some insights on the resonance assisted phenomenon, we have also included in our survey the corresponding saturated analogues (structures **2-MgH** and **2-OMgH** in Scheme **I**).

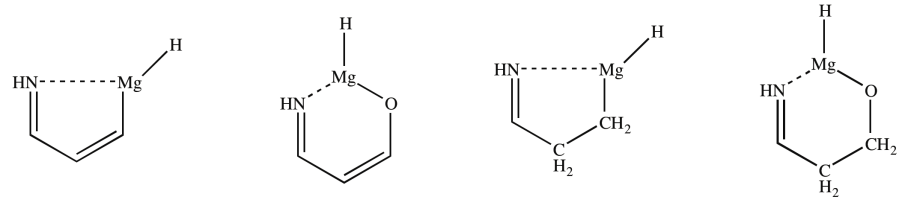


1 **1-MgH** **1-OMgH** **2-MgH** **2-OMgH**

Scheme I. Schematic representation of malonaldehyde (**1**) and the derivatives obtained by replacing its –OH group (**1-MgH**) or only the H atom of its –OH group (**1-OMgH**) by MgH. The corresponding saturated analogues (**2-MgH, 2-OMgH**) are also shown.

For the sake of completeness, and in order to break the symmetry of structures

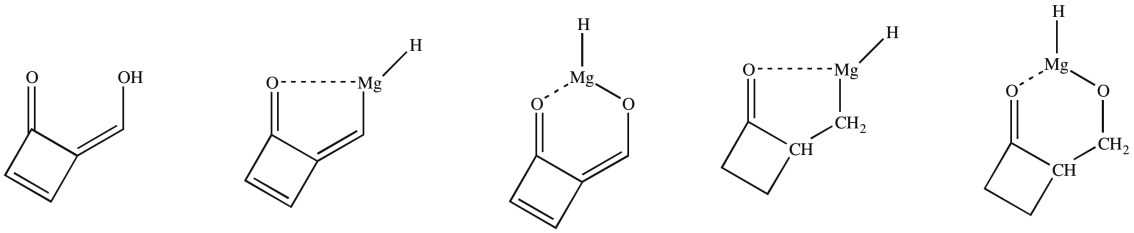
like **1-OMgH**, we also studied structures **3-MgH**, 3-**OMgH**, **4-MgH** and **4-OMgH** (see Scheme **II**) obtained by replacing the C=O group of the aforementioned malonaldehyde-like compounds by a C=NH group.



3-MgH **3-OMgH** **4-MgH** **4-OMgH**

Scheme II. Unsaturated and saturated systems obtained by replacing the carbonyl group of **1-MgH**, **1-OMgH**, **2-MgH**, **2-OMgH** by an –NH group.

Finally, in order to analyze the effect that a rigidity in the molecular framework may have on the characteristics of the intramolecular magnesium bond we included in our survey a third set of compounds derived from (*Z*)-4-(hydroxymethylene)cyclobut-2-enone (**5**) when its –OH group or only the H of its –OH group is replaced by a –MgH group (structures **5-MgH** and **5-OMgH** in Scheme **III**), along with the corresponding saturated analogues (structures **6-MgH** and **6-OMgH** in Scheme **III**).



5 **5-MgH** **5-OMgH** **6-MgH** **6-OMgH**

Scheme III. Schematic representation of (*Z*)-4-(hydroxymethylene)cyclobut-2-enone (**5**), and the derivatives obtained by replacing its –OH group (**5-MgH**) or only the H atom of its –OH group (**5-OMgH**) by MgH. The corresponding saturated analogues (**6-MgH, 6-OMgH**) are also shown.

Computational Details

The calculations of the systems under investigation were carried out using the Gaussian-4 (G4) theoretical approach [23]. The G4 theory is a composite model based on the use of B3LYP/6-311G(2df,p) optimized geometries. The same approach is employed to calculate the corresponding thermal corrections to the total energy, which

corresponds effectively to a CCSD(T,full)/G3LargeXP level of calculation plus a correction to the Hartree-Fock limit. This theoretical scheme is very well suited for the calculation of different thermodynamic magnitudes. Indeed, an assessment of the method on 454 experimental energies yielded an average absolute deviation from experiment of 3.47 $kJ.mol^{-1}$ [23].

To quantify the effects associated with the appearance of intramolecular interactions involving the Mg atom as acidic center, we firstly analyze the topology of the electron density of the different systems using the atoms in molecules (AIM) theory [24, 25]. In the AIM scheme, the topology of the electron density is characterized by the presence of (i) maxima, associated with the position of the nuclei, (ii) saddle points, located between two maxima or inside cyclic structures, named bond critical points (BCPs) and ring critical points (RCPs), respectively; and (iii) minima, associated with the existence of cage structures (CCPs). Also, it is possible to obtain the so called molecular graphs, which are formed by the ensemble of the bond paths, defined as the lines of maximum density connecting two maxima and containing a BCP. A second useful approach to analyze the electron density redistributions associated with this kind of interactions is the NBO method.[26] This approach permits to identify the interactions between occupied and empty orbitals within a given molecular system, either if they arise as the result of the interaction between two or more subunits, or as intramolecular interactions fostered by appropriate conformational changes. Since this method is based on the use of localized natural orbitals, it also permits to understand the bonding within the molecular framework in terms of hybrid bonding and antibonding orbitals and core and lone-pairs, obtained as local block eigenvectors of the one-particle density matrix. With this method is also possible to calculate the so-called Wiberg bond orders (WBOs) [27], which measure the strength of a chemical bond. A third approach is the ELF (Electron Localization Function) theory [28], which yields a useful partition of the molecular space into basins associated with the probability of finding electron pairs. These basins can be classified as disynaptic (polysynaptic) basins, when two (or more) atomic valence shells participate in it, and as monosynaptic, when associated to core electrons or lone-pairs.

Stabilizing or non-stabilizing non-covalent interactions (NCIs)[29] can be characterized by locating the regions in the three-dimensional space in which both the electron density and the reduced density gradient are low. In our study the regions in which NCIs are significant were located with the NCIPLOT code [29] and identified by

blue colors if they are strongly attractive, by red if they are strongly repulsive and by green if they are weak.

Results and Discussion

The G4-optimized structures of **1-MgH**, **1-OMgH**, **2-MgH** and **2-OMgH** are shown in Figure **1**, together with their molecular graphs. The first conspicuous fact is the existence of a BCP in the C=O···Mg bonding region with a sizable electron density. This permits to conclude that, in all cases, we can talk of the existence of a stabilizing intramolecular interaction between the Mg atom and the oxygen of the carbonyl group of the systems under investigation. It can be also observed that the shortest O···Mg distance is found for the **1-OMgH** derivative, which coherently presents the largest electron density at the O-Mg bond critical point (BCP).

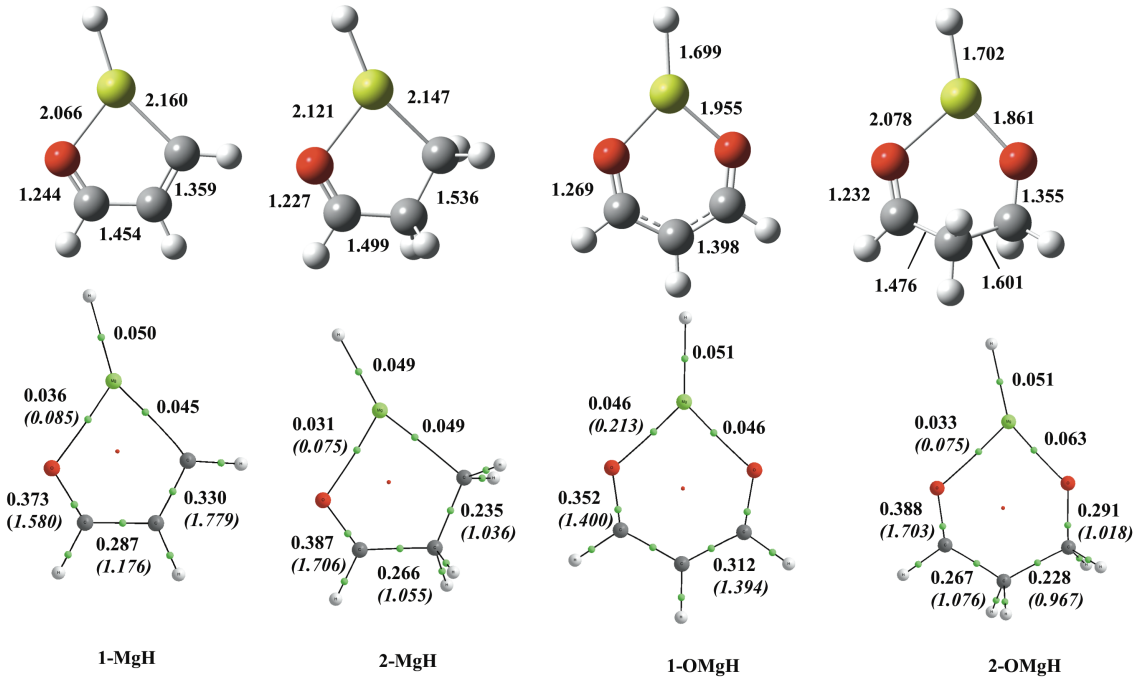
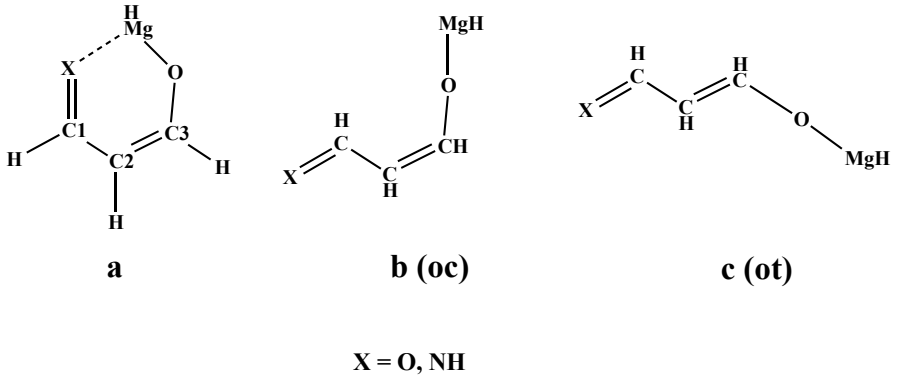


Figure 1. G4-optimized structures and molecular graphs of the **1-MgH**, **1-OMgH**, **2-MgH** and **2-OMgH** derivatives. Bond lengths are in Å. In the molecular graphs green and red dots denote BCPs and RCPs, whose electron densities are given in a.u. The values of the WBOs are shown in italics within parenthesis.

It can be also observed that the intramolecular O···Mg magnesium bond is weaker for the **1-MgH** and the **2-MgH** derivatives than for the oxygen containing analogues, **1-OMgH** and **2-OMgH**, respectively, as reflected in both the electron

density at the BCPs and the WBO of the linkage. For the **1-MgH**/**1-OMgH** couple, where the effect is stronger than for the **2-MgH**/**2-OMgH** one, this is the result of two concomitant features, the higher basicity of the C=O group and the higher intrinsic acidity of the MgH group of the **1-OMgH** derivative with respect to those of the **1-MgH** analogue. Indeed, our calculations at the G4 level, show that the intrinsic basicity of the carbonyl group of **1-OMgH**, measured by its proton affinity, is 78 kJ.mol^{-1} larger than that of the carbonyl group of **1-MgH**. Along with that, the intrinsic acidity of the –MgH group of the **1-OMgH** compound, measured by its hydride affinity calculated at the G4 level of theory, is also higher (by 48 kJ.mol^{-1}) than that of the **1-MgH** analogue.

An open question now is whether the enhanced strength of the O···Mg intramolecular bond in **1-OMgH** with respect the same interaction in the corresponding saturated counterpart, **2-OMgH**, is a consequence of a resonance-assisted phenomenon or not. To answer this question and tracing the origin of the stabilizing effect of the intramolecular magnesium in Schemes **I-III**, it is necessary to define a reference in which resonance is absent or minimum. Hence, for this purpose, we have included in our theoretical survey not only the aforementioned cyclic structures (**a** in Scheme **IV** for the **1-OMgH** compound taken as a suitable example), but also the open arrangements obtained by adequate internal rotations around the C-C bonds of these systems (structures **b** and **c** in Scheme **IV**). The **b** structure (that will be named by adding a **oc** (open *cis*) to the name of the cyclic compound) is generated by the internal rotation around the C1-C2 bond, and structure **c** (that will be named adding **ot** (open *trans*) to the name of the cyclic form) by a further rotation around the C2-C3 bond. Similar arrangements can be defined for the corresponding saturated analogues.



a **b (oc)** **c (ot)**

X = O, NH

Scheme IV. Conformers **oc** (open *cis*) and **ot** (open *trans*) which can be obtained from the cyclic conformer **a**, by successive rotations around the C1-C2 and C2-C3 bonds.

In Figure **2** we compare the structure, relative stabilities and molecular graphs of the different conformers of malonaldehyde (**1**) with those of **1-OMgH**. In both cases the global minimum corresponds to the cyclic structure, stabilized through an intramolecular O-H···O hydrogen bond in the case of malonaldehyde and through an intramolecular O-Mg···O magnesium bond in the case of the **1-OMgH** derivative.

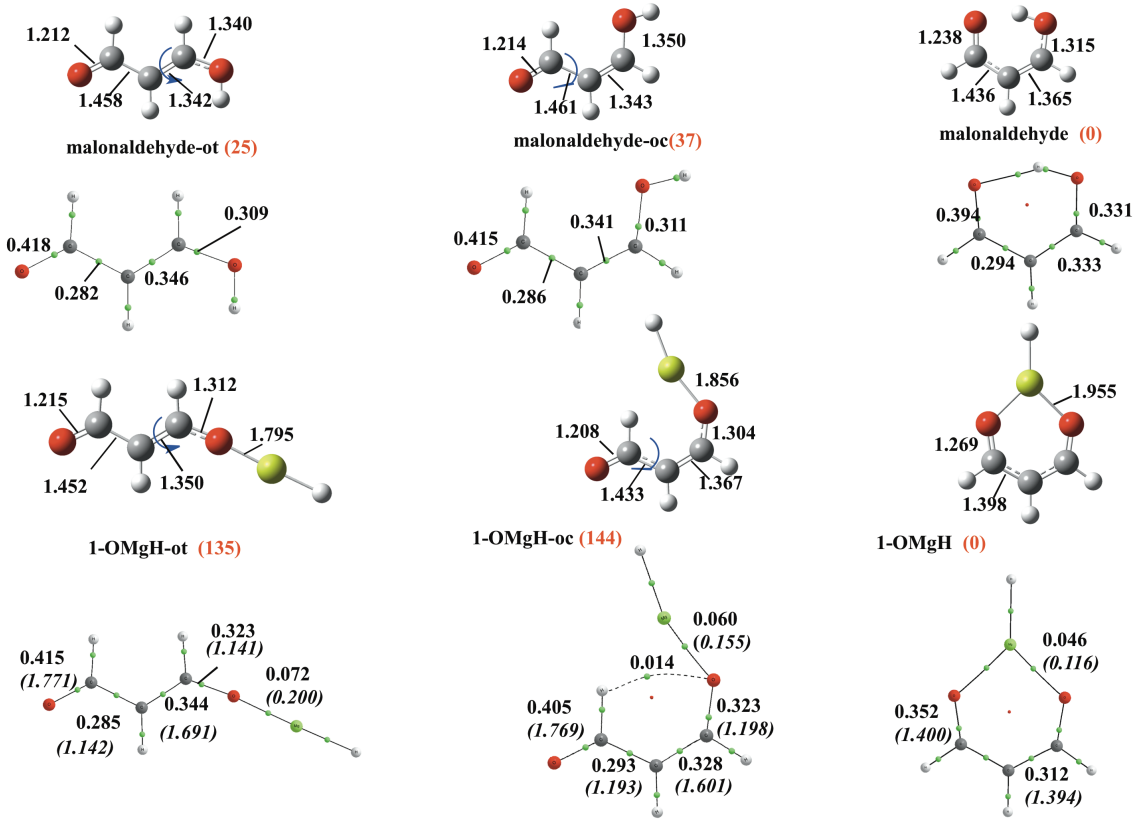
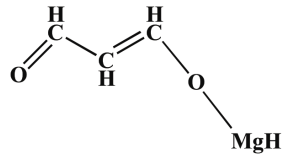


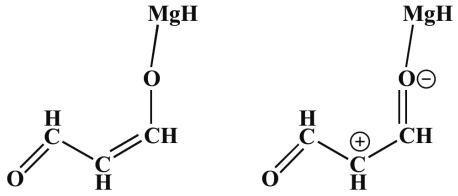
Figure 2. G4-optimized structures and molecular graphs of malonaldehyde and **1-OMgH** derivatives in their **ot** and **oc** conformations and in the cyclic global minimum. The curved blue arrows in structures **ot** and **oc** indicate the rotations around the C2-C3 and C1-C2 needed to reach the cyclic global minimum (see text). Bond lengths are in Å. Green and red dots denote BCPs and RCPs, respectively, whose electron densities are given in a.u. WBOs are also given in italics and within parenthesis. The relative energies (in kJ·mol^{-1}) with respect to the cyclic global minima are shown in red next to the name of the system.

For both **1** and **1-OMgH** the most localized structure corresponds to the **ot** conformer. As a matter of fact, as shown in Scheme **V**, for the **ot** conformer only one resonant structure is located by the NBO analysis, meaning that any other resonant form has a negligible weight with respect to the one shown in Scheme **V**.

1-OMgH-ot

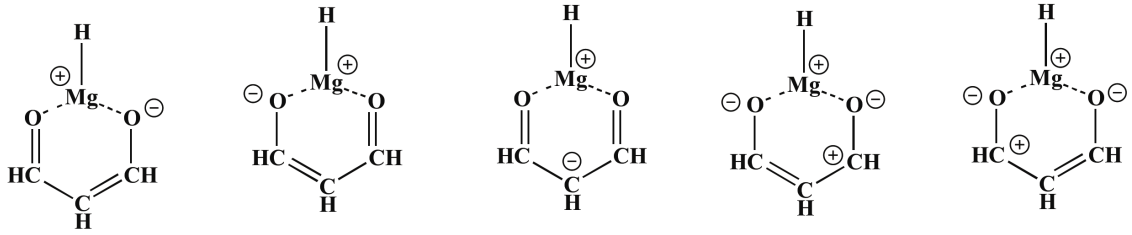


1-OMgH-oc



50 21

1-OMgH



24 24 21 10 10

Scheme V. Dominant resonant forms, with their relative % weights for **1-OMgH-ot**, **1-OMgH-oc** and **1-OMgH** conformers.

Conversely the oc conformer presents, as illustrated in Scheme V, the contribution of two dominant resonant structures, favoring a certain delocalization which results in closer values of both the electron densities at the BCPs and the WBOs of the C1-C2 and C2-C3 bonds. Both indexes also indicate that the delocalization extends also to the C-OMg bond, which is coherent with the participation of the two resonant structures of Scheme V. These features are responsible for the bifurcated bond path found in 1-**OMgH-oc** (Figure 2). We will come back to this point later on.

The delocalization, as expected, increases further on going from the **oc** conformer to the cyclic global minimum, as evidenced by the significant number of contributed forms in the third row of Scheme **V**. However, this factor is not necessarily the one that dictates the enhanced stability of the cyclic form. Indeed, on going from the **ot** to the **oc** conformer the stability of the system decreases, even though the resonance increases, as

just mentioned. This seems to indicate that, as it was claimed before in the literature, the enhanced stability of the cyclic form is not a consequence of a resonance-assisted phenomenon. Conversely, what is evident from these results is that the formation of the intramolecular hydrogen bond, in the case of malonaldehyde, or the formation of the intramolecular magnesium bond, in the case of the **1-OMgH** derivative, leads to a greater resonance in the system. In other words, we observe not a resonance-assisted intramolecular interaction but, as previously reported,[15-18] a resonance enhancement favored by the appearance of the intramolecular interaction, which for the case of intramolecular hydrogen bonds, was named hydrogen-bonding-assisted resonance (HBAR) [17]. Actually, this is the only way to explain why in the case of malonaldehyde the H atom is not symmetrically located between both oxygen atoms, whereas the **1-OMgH** derivative exhibits a clear C_{2v} symmetry. If the strength of the intramolecular hydrogen bond would truly reflect a RAHB phenomenon the minimum in malonaldehyde should correspond to the structure with maximum resonance, i.e., to the symmetric structure. This only happens in the **1-OMgH** compound simply because, as discussed above, the carbonyl group exhibits a higher intrinsic basicity than that of malonaldehyde and the MgH group exhibits a very high intrinsic acidity, both factors leading to a very strong O-MgH interaction.

Nonetheless, the intramolecular O···MgH bond is stronger in the unsaturated **1-OMgH** than in its saturated counterpart **2-OMgH**. This difference is again due to the different intrinsic basicities of the C=O groups of both systems and the different intrinsic acidities of their –MgH groups. Our G4 estimates indicate that the carbonyl group of the **1-OMgH-ot** compound has a proton affinity 110 kJ.mol^{-1} higher than that of the **2-OMgH-ot** saturated analogue. Similarly, the hydride affinity of the –MgH group of the former is 65 kJ.mol^{-1} higher than that of the latter.

If we replace the carbonyl basic site in **1-OMgH** by a –CNH imino group to give **3-OMgH**, the general panorama described above does not change significantly, though the symmetry of the cyclic structure necessarily decreases. As shown in Figure **3**, the energy gap between the cyclic conformation and the **ot** open form is slightly larger for **3-OMgH**, just reflecting that the intrinsic basicity of the C=NH group of **3-OMgH-ot** (1018 kJ·mol^{-1}) is larger than that of the carbonyl group of the **1-OMgH-ot** analogue (922 kJ·mol^{-1}). However, as found for the **1-OMgH** derivative, although the resonance slightly increases on going from **3-OMgH-ot** to **3-OMgH-oc** as shown by the electron densities and the WBOs, the stability of the system does not.

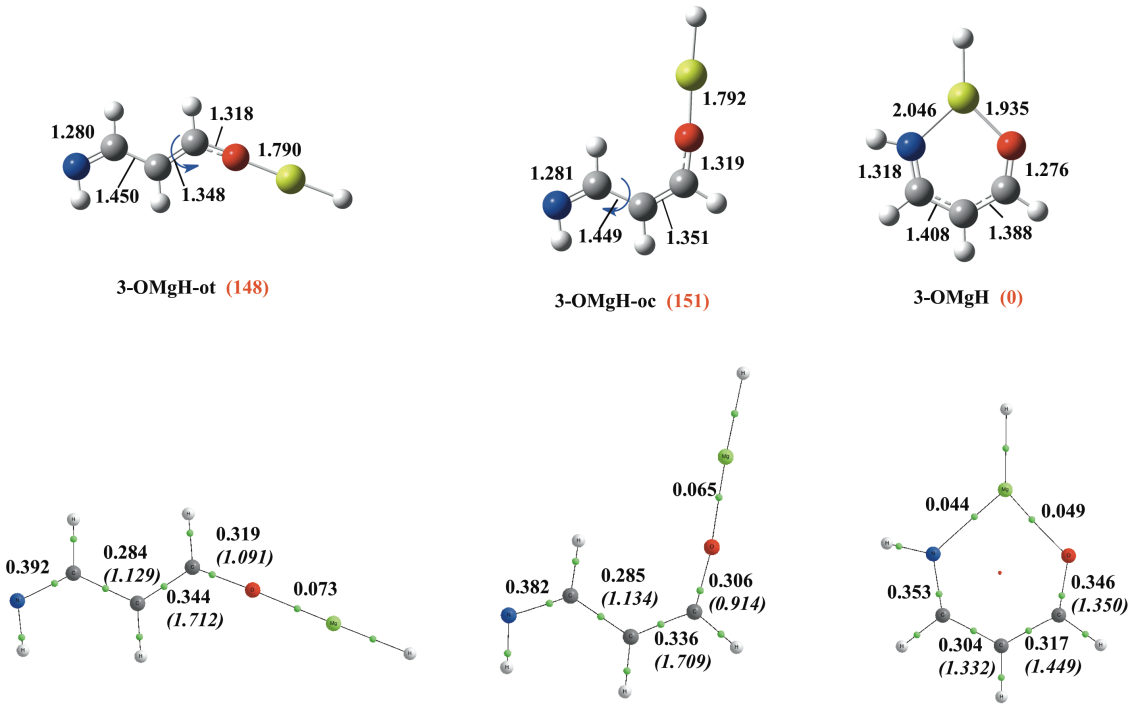


Figure 3. G4-optimized structures and molecular graphs of **3-OMgH** derivative in its **oc** and **ot** conformations and in the cyclic equilibrium structure, obtained by suitable rotations around the C2-C3 and C1-C2 bonds (see text). Bond lengths are in Å. Green and red dots denote BCPs and RCPs, respectively, whose electron density is given in a.u. WBOs are also given in italics and within parenthesis. The relative energies (in kJ·mol^{-1}) with respect to the cyclic global minima are shown in red next to the name of the system.

There are some subtle differences, however, as far as the structures of the **oc**-conformers of **1-OMgH** and **3-OMgH** are concerned. As it can be easily seen by comparing Figures **2** and **3**, the C-O-Mg arrangement in **3-OMgH-oc** is strictly linear whereas the C-O-Mg angle is 134.8º in **1-OMgH-oc**. The origin of these structural differences can be rationalized by looking at the NCIs (see Figure **4**), which allows visualizing the interactions of interest in the three-dimensional space. The NCI representation clearly shows that whereas on structure **1-OMgH-oc** there is an area of repulsive NCI between the CH group and the oxygen atom attached to Mg, and an attractive one between this H atom and the Mg atom, in **3-OMgH-oc** only the former remains. Note that the NCI characteristics of the **1-OMgH-oc** are fully consistent with the presence of the bifurcated bond path found for this structure in Figure 2. This picture is consistent with the features of the ELF in the same areas, where the density around the O atom is clearly polarized towards the H atom in the **1-OMgH-oc** compound, with one disynaptic basin and another monosynaptic one, whereas for **3-**

OMgH-oc this polarization is not observed and only a disynaptic O-Mg basin is found. In agreement with this, the population of the C-H disynaptic basin is larger for the 1-OMgH-t compound than for the **3-OMgH-oc** analogue, and the C-H distance is 0.055 Å longer. The NBO analysis also shows that whereas for the **3-OMgH-oc** there is no interaction whatsoever between the CH and the MgH groups, for the **1-OMgH-oc** there is an interaction between σ_{CH} bonding orbital and the empty *3p* Mg orbitals and the σ_{MgH}* antibonding orbital. Consistently, the WBO between this H and Mg is zero for the **3-OMgH-oc**, but 0.09 for the **3-OMgH-oc** derivative. The first orbital interaction is responsible for the bending of the O-Mg-H arrangement (bond angle 161.8º), because of the population of the *3p* orbitals of Mg changes its hybridization. The second results in a slight lengthening of the Mg-H bond (0.013 Å) with respect to the **ot** conformation.

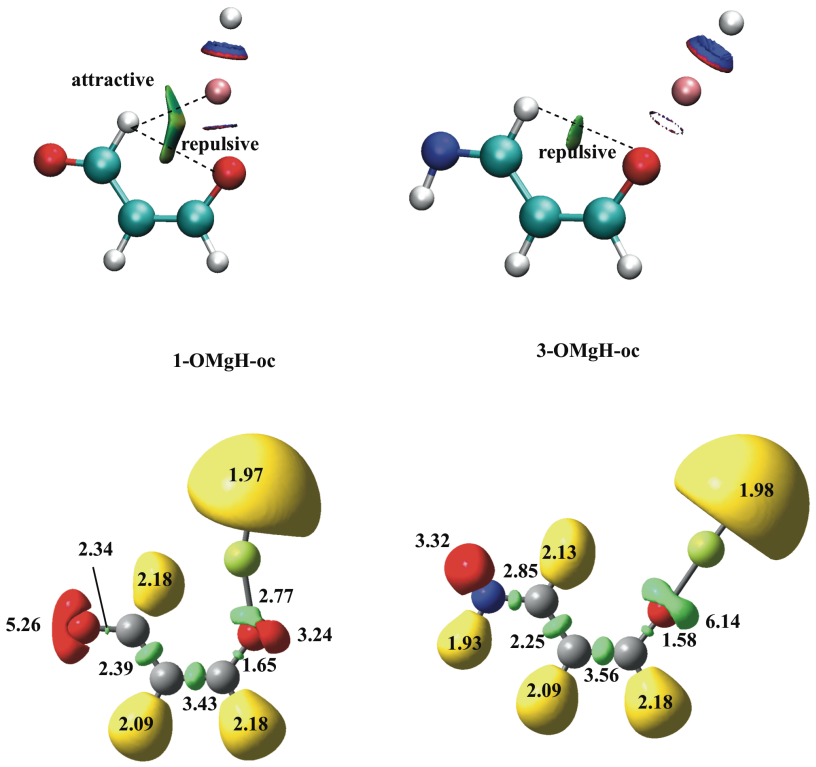


Figure 4. The first row shows NCI areas for both compounds. The second row shows the ELF plots of the **1-OMgH-oc** and **3-OMgH-oc**. Yellow, red and green lobes correspond to chemical bonds involving hydrogen atoms, monosynaptic basins associated with lone pairs, and disynaptic basins corresponding to chemical bonds between heavy atoms. Populations in e are indicated.

The differences between the saturated **3-OMgH** and the unsaturated **4-OMgH** derivatives have the same origin as those discussed above between **1-OMgH** and **2-**

OMgH. Indeed, our G4 calculations show that the HN···Mg intramolecular interaction is stronger in **3-OMgH** than in **4-OMgH**, but again this just reflect the fact that the intrinsic acidity of the –NH group of **3-OMgH-ot** (G4 proton affinity 1018 kJ·mol^{-1}) is sizably larger than that of the saturated analogue (G4 proton affinity 947 kJ·mol^{-1}). At the same time, the intrinsic acidity of the –MgH group of **3-OMgH-ot** (G4 hydride affinity 366 kJ·mol^{-1}) is also higher than that of **4-OMgH-ot** (G4 hydride affinity 317 kJ·mol^{-1}). Hence, unavoidably the intramolecular N···Mg interaction should be stronger in **3-OMgH-ot** than in **4-OMgH-ot** not as a consequence of a resonance assisted phenomenon, but as a result of the differences in the intrinsic reactivity of the two active groups.

When some rigidity is introduced in the **1-OMgH** system by fusing the malonaldehyde-like moiety to a four-membered ring to yield **5-OMgH**, significant changes appear. For the sake of an easier comparison we have reproduced again the structure of the **1-OMgH** compound below that of **5-OMgH** in Figure **5**.

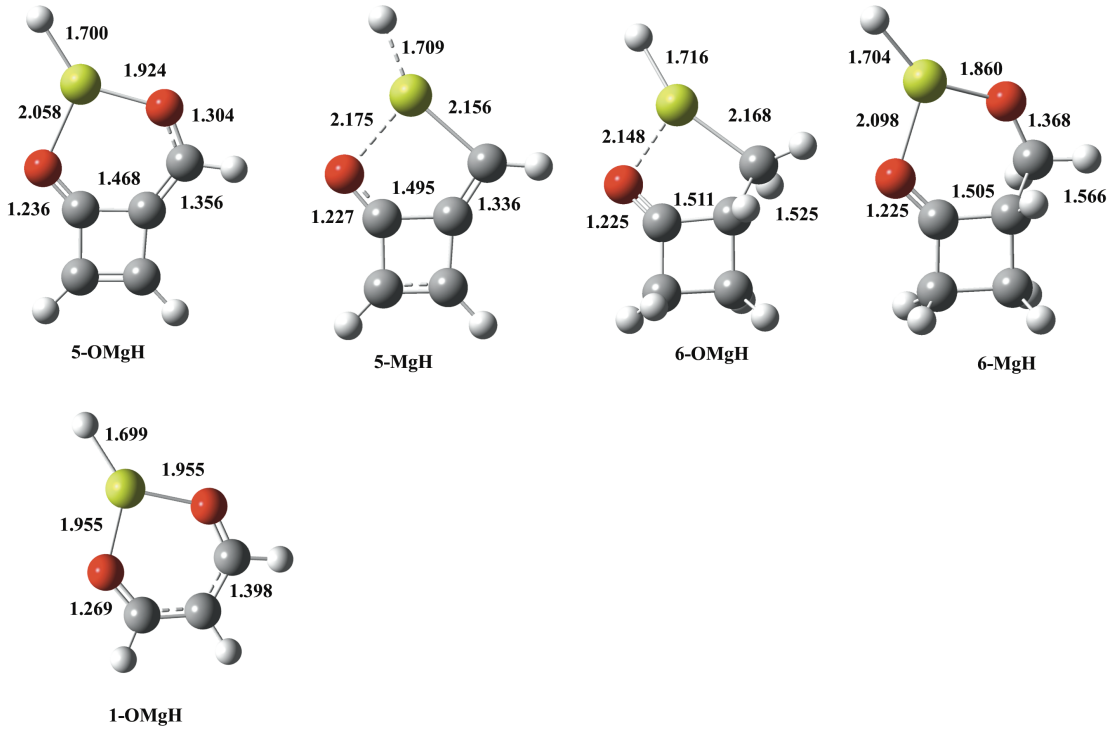


Figure 5. G4-optimized structures and molecular graphs of the **5-OMgH**, **5-MgH**, **6-OMgH**, **6-MgH** derivatives in their equilibrium conformations. Bond lengths are in Å.

The first obvious effect on going from **1-OMgH** to **5-OMgH** is a decrease in the symmetry of the system, as the two CO groups in **5-OMgH** are no longer in the same

environment. It is obvious that in **1-OMgH** the two carbonyl groups belong to aldehyde functions, whereas in **5-OMgH** one of them is now a keto group. However this is not the main factor as shown by the very small differences observed when one of the aldehyde functions of the **1-OMgH** system is changed into a keto group by substituting the H atom of one of the aldehyde functions by a methyl group (See Figure 1 of the Supporting Information). The important finding is that no resonance is observed, although in principle some effect in this sense could be expected. Indeed, the C=O bond attached to the four-membered ring in **5-OMgH** is much shorter than the C=O bonds in **1-OMgH**, whereas the other is much larger. The O···Mg intramolecular interaction is also much weaker in **5-OMgH** than in **1-OMgH**, but again, this is a direct consequence of the changes in the intrinsic reactivity of the centers involved. In fact, our G4 calculations show that the basicity of the carbonyl group in the **5-OMgH-oc** conformer is 58 $kJ \cdot mol^{-1}$ smaller than that of **1-OMgH-ot,** and the hydride affinity of the MgH group is also smaller by 30 $kJ \cdot mol^{-1}$. This implies that the charge transfer from the carbonyl lone-pairs into the empty orbitals of the –MgH group should be smaller in **5-OMgH** than in **1-OMgH**, and indeed this is the case. Whereas for **1-OMgH** the interaction energy between the lone-pairs of the O atom and the σ_{MgH}* antibonding orbital is 125 $kJ \cdot mol^{-1}$, for **5-OMgH** is only 96 $kJ \cdot mol^{-1}$. The same trend is observed when the interactions with the empty *p* orbitals of Mg are concerned, but the fact that the orbital interactions associated with the formation of the O···Mg intramolecular bond are weaker in **5-OMgH** implies that the perturbation of the electron density distribution of the rest of the molecule is also weaker. Consequently, whereas the formation of the **1-OMgH** cyclic conformer, implies a lengthening of the C=O and the C=C bonds of 0.054 Å and 0.048 Å, respectively, for **5-OMgH** these lengthenings are only 0.037 Å and 0.018 Å, respectively.

The final question that deserves to be discussed is whether the characteristics of these intramolecular interactions differ significantly when Mg is replaced for Be. For this purpose we have chosen as a suitable model system the **1-OMgH** compound to be compared with the Be-containing analogue, namely **1-OBeH**. The G4-structure of the most stable cyclic conformer and that of the **1-OBeH-oc** form were taken form ref. [9]. These two Be structures together with **1-OBeH-ot** are shown in Figure **6**. The corresponding molecular graphs are also given.

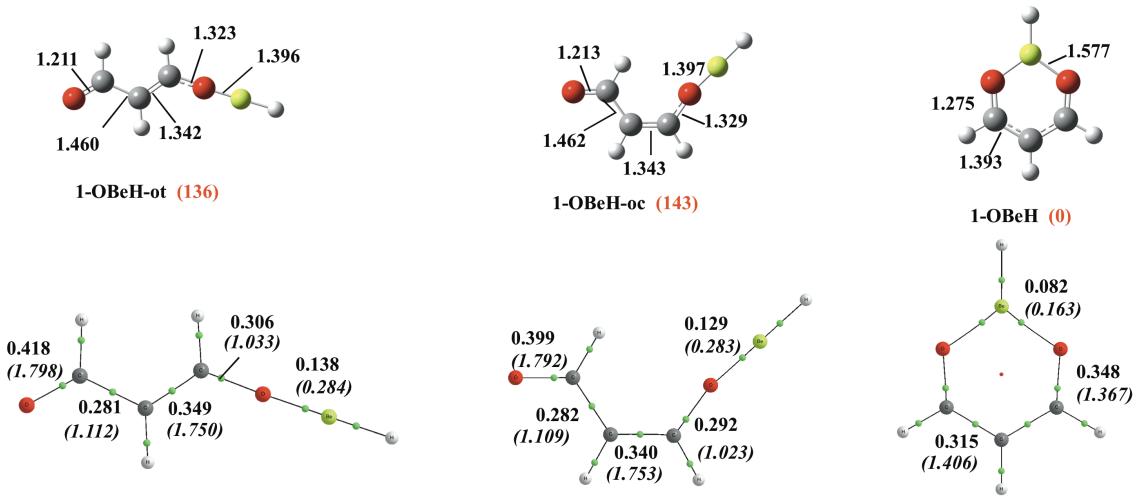


Figure 6. G4-optimized structures and molecular graphs of **1-OBeH** for its **ot** and **oc** conformations and for its cyclic global minimum. Bond lengths are in Å. Green and red dots denote BCPs and RCPs, respectively, whose electron densities are given in a.u. The WBOs are also shown in italics and within parenthesis. The relative energies (in $kJ \cdot mol^{-1}$) with respect to the cyclic global minima are shown in red next to the name of the system.

A comparison of Figure **6** with the two bottom lines of Figure **2** shows that all bond distances in all the three pairs **1-OBeH/1-OMgH, 1-OBeH-oc/1-OMgH-oc, 1-OBeH-ot/1-OMgH-ot** are similar but not equal, with the only exception of the O-Be and O-Mg bonds. Actually, the net NBO charges at Be and Mg in **ot** conformers are 1.37 and 1.48, respectively, meaning that the charge transfer from the molecular frame to the–BeH group in **1-OBeH** conformers is slightly larger than for the Mg containing analogue. Coherently, a closer analysis of the data (bond lengths, electron densities at the BCPs and the WBOs) shows that the changes on going form the **ot** conformer to the cyclic global minimum are slightly larger in the case of the Be derivatives. Taken the C=O bond as an illustration, the bond length, electron density and WBO in the Be-containing system change on going from the **ot** conformer to the cyclic structure by 0.064 Å, 0.070 a.u., 0.431, whereas for the Mg analogue the changes are 0.054 Å, 0.063 a.u. and 0.371, respectively. These results seem to indicate that the differences between Be and Mg are marginal. As a matter of fact, the energy gaps between the cyclic global minimum and the open **oc** and **ot** conformers are essentially the same for both Be and Mg-containing derivatives (see Figures **2** and **6**). Rather interestingly, these findings are consistent with the conclusions of very recent papers pointing out the strong similarity between Be and Mg systems as far as their behavior is concerned. Torvisco and Ruhlandt-Senge showed [30] that Be and Mg display rather similar high charge/size ratios favoring the formation of linkages with a high covalent character, which are never

observed for Ca or other heavier alkaline-earth elements. Later, Montero-Campillo et al. showed [22], at the same level of theory used in this work, that Mg derivatives induce acidity enhancements as large as those observed for the Be-containing analogues. Very recently, the same authors found that cyclopropane Mg derivatives exhibit intrinsic anion affinities of the same order or even larger than those predicted for the Be-containing analogues.

Concluding Remarks

In this study we have found that all the compounds under investigation present as a global minimum of the potential energy surface a cyclic structure stabilized through the formation of rather strong intramolecular magnesium bonds. Although the energy of an intermolecular interaction can be calculated just by evaluating the energies of the interacting systems and that of the global compound, the strict quantitative evaluation of an intramolecular interaction is not possible. In our case we have use as an indication of this strength the energy difference between the global cyclic minimum and the totally extended conformer that we named **ot**. These energy differences are always around 130-150 $kJ.mol^{-1}$, a clear indication of the high stability of the intramolecular magnesium bonds. Our analysis of the bonding also indicates that the strength of these interactions depends on both the intrinsic basicity of the carbonyl group (or the imino group) of the systems investigated and the intrinsic acidity of the –MgH group. No correlation was found however with any resonance assistance phenomenon. Indeed, the less stable **oc** conformers exhibit more resonance than the totally extended conformer **ot**, but they are systematically less stable. We conclude therefore that the resonance observed in the cyclic conformer is directly correlated with the strength of the intramolecular magnesium bond and not vice-versa, in what we could call named a magnesium-bonding-assisted resonance (MgBAR). When the carbonyl group is replaced by an imino group the strength of the intramolecular Mg-bond increases slightly, but the general bonding characteristics do not change significantly, as they do not change dramatically when some rigidity is introduced through the fusion of the malonaldehyde-type fragment to a unsaturated or saturated four-membered ring. Also interestingly, the strength and characteristics of these interactions for these Mg-containing derivatives are very similar to those of the corresponding Be-containing analogues.

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